

Identification of radiolytic products of [C₄mim][PF₆] under γ -irradiation*AO Yin-Yong (敖银勇),¹ XU Min (徐敏),¹ PENG Jing (彭静),¹LI Jiu-Qiang (李久强),¹ ZHAI Mao-Lin (翟茂林),^{1,†} and WU Guo-Zhong (吴国忠)^{2,‡}¹Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory for Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China²Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

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The trace water-soluble radiolytic products of neat 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) were identified by analysing water-washed samples of γ -irradiated ionic liquids. HF and difluorophosphoric acid were confirmed as the main radiolytic products of [C₄mim][PF₆], and their radiation chemical yields were quantified by ¹⁹F NMR ($G(F^-) = 0.14 \mu\text{mol/J}$, $G(\text{HOP}(\text{O})\text{F}_2) = 0.053 \mu\text{mol/J}$). Compared to [C₄mim][NTf₂], [C₄mim][PF₆] shows better radiation stability.

Keywords: [C₄mim][PF₆], γ -irradiation, Radiolytic products, Radiation chemical yields

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I. INTRODUCTION

The room-temperature ionic liquids (RTILs) are new-fashioned solvents and have too many attractive properties, especially in chemical stability and low vapour pressure, compared with traditional solvents. RTILs are considered promising solvents for the extraction of radioactive isotopes from spent nuclear fuel (SNF) [1–6]. This is an area of great significance to the nuclear industry, in which traditional volatile organic solvent extraction is currently used in SNF reprocessing and recycling. The solvent extractions of actinide metals were investigated using [C₄mim][PF₆], which showed that the use of [C₄mim][PF₆] greatly enhances metal ion partitioning, compared to using a traditional solvent [7]. A highly efficient extraction of Sr²⁺ from an aqueous solution can be achieved using [C₄mim][PF₆] in combination with crown ether [8, 9]. Sr²⁺ partitioning in the crown ether, combined with the [C₄mim][PF₆] extraction phase, decreased obviously after γ -irradiation [10]. The decline of the distribution ratio was attributed to the inhibition of the cation exchange mechanism and competition by radiation-formed hydrogen ions. However, γ -irradiation of [C₄mim][PF₆] showed no discernible influence on Sr²⁺ extraction from a nitric acid solution with high acidity [11]. This research shows the feasibility of [C₄mim][PF₆] as an extracting solvent for the reprocessing of SNF.

In an extraction process involving SNF, there will be a requirement for extracting agents and solvents to be robust to high radiation doses [12–14]. Therefore, studies on the radiation effects of RTILs are of great importance before their practical application in SNF reprocessing and recycling. Micro-FTIR, ¹H NMR, and ¹⁹F NMR spectra of [C₄mim][PF₆] irradiated at 550 kGy suggested that no dis-

cernible changes were found in these spectra [14, 15]. Qi *et al.* reported that the radiolysis of [C₄mim][PF₆] leads to an increase in UV-vis absorbance and a decrease in fluorescence intensity [12]. Radical generated species and different degradation pathways were proposed for imidazolium ionic liquids under electron irradiation and were confirmed by electron paramagnetic resonance [16–18]. The cation radical C₄mim^{•+}, neutral radical C₄mim[•], and other potential species were observed by pulse radiolysis during the irradiation of dry [C₄mim][PF₆] [19]. However, as of now there are still few works focusing on the identification of radiolytic products of [C₄mim][PF₆].

In this work, the aim of the present study is to report the identification of water-soluble radiolytic products of [C₄mim][PF₆] by using Micro-FTIR, ¹⁹F NMR, and ³¹P NMR. ¹⁹F NMR was employed to provide a quantitative study for the radiolytic products of [C₄mim][PF₆] and their radiation chemical yields were obtained.

II. MATERIALS AND METHODS

A. Materials

[C₄mim][PF₆] (>99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected by NMR analysis. Difluorophosphoric acid hemihydrate (HOP(O)F₂ · 5H₂O, Strem Chemicals, Inc.) was obtained as a standard compound for the identification of radiolytic products of [C₄mim][PF₆]. CF₃COONa (Tokyo Chemical Industry Co, >98%) was used for quantitative analysis. Other solvents were analytical-grade reagents and used without further purification.

B. Irradiation

The irradiation of [C₄mim][PF₆] ionic liquid was carried out in air ((298 ± 2) K) using a ⁶⁰Co source with an average

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dose rate of ca. 210 Gy/min (Department of Applied Chemistry of Peking University). The absorbed dose was traced by a Fricke dosimeter.

C. Identification of radiolytic products

The separation of water-soluble radiolytic products from the organic phase was conducted by contacting 0.5 mL of irradiated sample with 0.5 mL of deuterium oxide (D_2O) for about 10 min in a vibrating mixer, followed by centrifuging to ensure that the phases were fully contacted and separated. The aqueous phase from the wash of irradiated $[C_4mim][PF_6]$ was analysed by various spectroscopic methods.

Micro-FTIR: The aqueous phase was dropped onto a slide and dried at 40 °C for 30 min. Then, the residual radiolytic products on the slide were analysed by a Magna-IR 750 Thermo Scientific Micro Fourier transform infrared spectrometer (Micro-FTIR) in the spectral range of 4000–600 cm^{-1} .

NMR: The aqueous phase was analyzed by a Bruker 500 MHz Avance III NMR spectrometer. C_6F_6 (−162.73 ppm) for ^{19}F NMR and H_3PO_4 (0 ppm) for ^{31}P NMR spectra were used as references. CF_3COONa was dissolved in deuteriooxide (50 mmol/L) and used as internal standard compound for quantitative analysis.

III. RESULTS AND DISCUSSION

Micro-FTIR and 1H NMR spectra of $[C_4mim][PF_6]$ suggested that no discernible changes were found, even after irradiation at 550 kGy [14], which was an indication that the radiolytic species were very small in quantity. In order to separate water-soluble radiolytic products from the organic phase, the irradiated $[C_4mim][PF_6]$ was washed by D_2O and then the aqueous phase (A-phase) was analysed by various spectroscopic methods. As shown in Fig. 1, the absorption of A-phase shows some changes, compared to that of the unirradiated sample. The absorption of the unirradiated sample is attributed to $[C_4mim][PF_6]$ ionic liquid. For A-phase, an absorption band at 1521 cm^{-1} was attributed to a Lewis acid, which has been identified using pyridine as a molecular probe [10]. The absorption bands at 1299 cm^{-1} and 1140 cm^{-1} corresponded to the vibration of the $O=P-O$ bonds [20, 21], which indicate that the $P-F$ bond was broken and an $O=P-O$ bond was formed during the irradiation of $[C_4mim][PF_6]$. The change of absorption band at 841 cm^{-1} indicated the formation of a PF_2 group [21].

^{19}F NMR and ^{31}P NMR chemical shifts are highly sensitive to fluorine-containing and phosphorus-containing compounds, respectively. The A-phase was also analysed by ^{19}F NMR and ^{31}P NMR. As shown in Fig. 2, the ^{19}F NMR of the unirradiated sample shows a duplicate peak at −71.70 ppm ($J_{F-P} = 706.5$ Hz) assigning to PF_6^- . The A-phase shows two new peaks at −82.60 (duplicate, $J_{F-P} = 960.8$ Hz) and −129.58 ppm, which were ascribed to the signals of the radiolytic products. The chemical shifts at −129.58 ppm can be assigned to the signal of HF, which has been identified

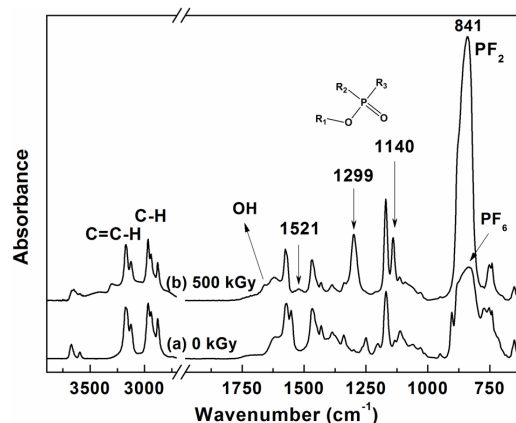


Fig. 1. Micro-FTIR spectra of unirradiated and irradiated $[C_4mim][PF_6]$ (The aqueous phase from the washing of unirradiated sample (a) and γ -irradiated sample (b)).

as a main radiolytic product of $[C_4mim][NTf_2]$ [22, 23]. HF fumes were also detected during the irradiation of $[C_4mim][PF_6]$ [12], thus, HF was one of main radiolytic products of $[C_4mim][PF_6]$.

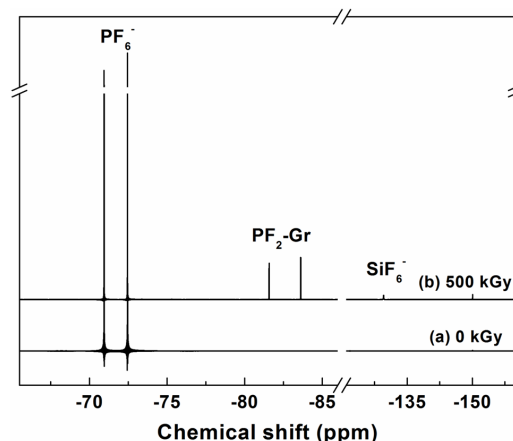


Fig. 2. ^{19}F NMR spectra of unirradiated and irradiated $[C_4mim][PF_6]$ (The aqueous phase from the washing of unirradiated sample (a) and γ -irradiated sample (b)).

As shown in Fig. 3, the ^{31}P NMR of an unirradiated sample shows a heptet at −145.01 ppm ($J_{F-P} = 707.0$ Hz) assigning to PF_6^- . A new triplet at −14.82 ppm is observed in the A-phase. Combined with the results of ^{19}F NMR, the triplet at −14.82 ppm ($J_{F-P} = 959.7$ Hz) has the same coupling constants as the peak at −82.60 ppm in ^{19}F NMR ($J_{F-P} = 960.8$ Hz), which indicates that the chemical structure of the radiolytic product contains a PF_2 group (PF_2-Gr). Lu *et al.* pointed out that $[OP(O)F_2]^-$ was one of the hydrolysis products of $[C_4mim][PF_6]$ [24]. $HOP(O)F_2$ is a possible radiolytic product when $[C_4mim][PF_6]$ is irradiated by γ -radiation. A $HOP(O)F_2$ standard compound was obtained for further identification. The $HOP(O)F_2$ shows a duplicate peak at −82.64 ppm ($J_{F-P} = 961.4$ Hz) in ^{19}F NMR and a

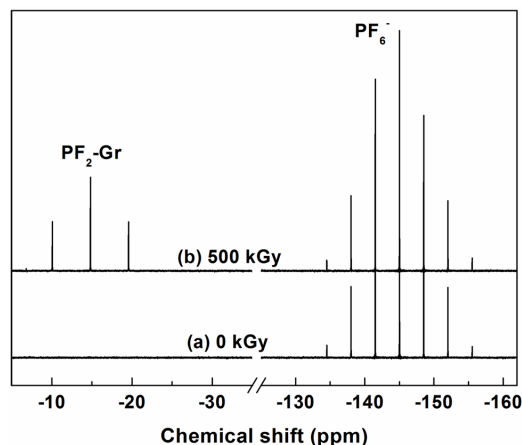


Fig. 3. ^{31}P NMR spectra of unirradiated and irradiated $[\text{C}_4\text{mim}][\text{PF}_6]$ (The aqueous phase from the washing of unirradiated sample (a) and γ -irradiated sample (b)).

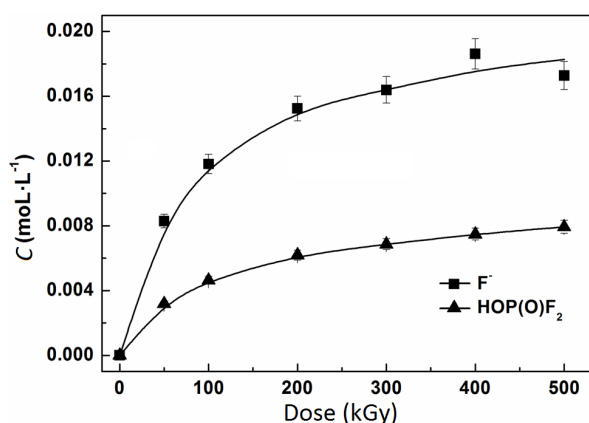


Fig. 4. The relationship between the concentration of radiolytic products and doses.

triplet at -14.85 ppm ($J_{\text{F-P}} = 961.4$ Hz) in ^{31}P NMR, we can conclude that the radiolytic product $\text{PF}_2\text{-Gr}$ can be definitely confirmed as $\text{HOP}(\text{O})\text{F}_2$.

According to the above results, HF and $\text{HOP}(\text{O})\text{F}_2$ are confirmed as the main radiolytic products of $[\text{C}_4\text{mim}][\text{PF}_6]$ under γ -irradiation. In order to realize a quantitative anal-

ysis of the radiolytic products of $[\text{C}_4\text{mim}][\text{PF}_6]$ after γ -irradiation, herein, the irradiated sample was washed 4 times with D_2O before analysis to ensure that acidic radiolytic products were totally collected. After 4 washes, a neutral upper aqueous phase was obtained and analysed by ^{19}F NMR. CF_3COONa was dissolved in deuterioxide (50 mmol/L) and used as an internal standard compound for the quantitative analysis. Compared to the unirradiated sample, the amounts of main radiolytic products increased obviously with dose increases (Fig. 4). The radiation chemical yields of radiolytic products ($G = G(\text{F}^-) + G(\text{HOP}(\text{O})\text{F}_2) = 0.14 \mu\text{mol/J} + 0.053 \mu\text{mol/J} = 0.19 \mu\text{mol/J}$) are close to the radiation chemical yields of the anion ($0.18 \mu\text{mol/J}$) of $[\text{C}_4\text{mim}][\text{PF}_6]$ determined by ^{19}F NMR [25]. Compared to the radiation chemical yields of acidic radiolytic products of $[\text{C}_4\text{mim}][\text{NTf}_2]$ (Table 1), the radiation stability of $[\text{C}_4\text{mim}][\text{PF}_6]$ is better than that of $[\text{C}_4\text{mim}][\text{NTf}_2]$ and is influenced by the chemical structure of the anion. HF and $\text{HOP}(\text{O})\text{F}_2$ were identified as the main radiolytic products of PF_6^- of $[\text{C}_4\text{mim}][\text{PF}_6]$, and their overall contents were less than 0.7% for $[\text{C}_4\text{mim}][\text{PF}_6]$, even when irradiated at 500 kGy.

TABLE 1. Radiation yields of radiolytic products and corresponding anions

RTILs	$G(\text{F}^-)$	Other products ($\mu\text{mol/J}$)	$G(\text{anion})$ ($\mu\text{mol/J}$)
$[\text{C}_4\text{mim}][\text{PF}_6]$	0.14	0.053	-0.18 [25]
$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.20 [22]	0.151 [22]	-0.22 [25]

IV. CONCLUSION

The trace water-soluble acidic radiolytic products of $[\text{C}_4\text{mim}][\text{PF}_6]$ were confirmed by using various spectroscopic methods, including Micro-FTIR, ^{19}F NMR, and ^{31}P NMR. The main radiolytic products (HF and $\text{HOP}(\text{O})\text{F}_2$) of $[\text{C}_4\text{mim}][\text{PF}_6]$ were identified and their amount was quantified by ^{19}F NMR. The overall concentration of non-volatile acidic radiolysis products was less than 0.7% for $[\text{C}_4\text{mim}][\text{PF}_6]$, even when irradiated at 500 kGy, which shows that $[\text{C}_4\text{mim}][\text{PF}_6]$ has excellent radiation stability and is promising for the application of extractions in nuclear fuel reprocessing.

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